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PHOTOINITIATED DOPING OF POLYACETYLENE. (U)
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OFFICE OF NAVAL RESEARCH

Contract 15 N00014-80-C-0779

Technical Report No 19 1-2

Photoinitiated Doping of Polyacetylene

(10)

by

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Prepared for Publication

DTIC
SELECTED
S A 03 1981

in the

Journal of the Chemical Society

Chemical Communications

IBM Research Laboratory
5600 Cottle Rd.
San Jose, CA 95193

July 28, 1981

7/28/81

6/2

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RJ3037 (37672) 1/28/81
Chemistry

PHOTOINITIATED DOPING OF POLYACETYLENE

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ABSTRACT: Ultraviolet irradiation of polyacetylene films treated with diaryliodonium or triarylsulfonium salts leads to doping of the exposed areas and provides greater control of the doping process than can be achieved by conventional doping methods.

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Polyacetylene, $(CH)_x$, has attracted considerable attention over the past three years because of its unique electronic properties. Although $(CH)_x$ is intrinsically a wide band gap semiconductor, its conductivity can be systematically varied over twelve orders of magnitude from 10^{-9} to 10^3 $\text{ohm}^{-1}\text{-cm}^{-1}$ by treatment with a variety of oxidizing or reducing agents.¹ An important prerequisite to the use of polyacetylene in device-type applications, however, is the ability to selectively dope specific areas of a film in order to generate conducting or semiconducting patterns. Simple dopant diffusion techniques using conventional masks are not applicable due to the highly porous nature of these films.² Attempts to dope $(CH)_x$ by ion implantation have produced mixed results.³ We report here a solution to this problem using as dopants triarylsulfonium or diaryliodonium salts, species which are normally inert toward polyacetylene, but which on irradiation undergo photochemical reaction leading to doping of the polymer.

The search for materials whose photoproducts are effective dopants was aided by the discovery by Gau et al. that proton acids are capable of doping $(CH)_x$.⁴ Crivello and Lam had previously shown that triarylsulfonium and diaryliodonium salts decompose on ultraviolet irradiation to produce the corresponding proton acids.^{5,6} We now find that the conductivities of $(CH)_x$ films impregnated with, for example, triphenylsulfonium hexafluoroarsenate can be raised to approximately $2 \text{ ohm}^{-1}\text{-cm}^{-1}$ on exposure to ultraviolet radiation, presumably as a result of proton doping. Diphenyliodonium hexafluoroarsenate proves equally effective. Irradiation of pristine $(CH)_x$ under identical conditions produces no change in conductivity or composition. (All irradiations were carried out in a Rayonet reactor at 254 nm. Conductivities were measured by the four point probe method using either pressed contacts or gold leads evaporated onto the film before treatment with the salt.)

Since polyacetylene itself has some absorption at 254 nm, the penetration of light into the film and the resulting doping process should be a function of both film thickness and irradiation time. Figure 1 shows the conductivity of a 50 micron thick film as a function of exposure time (both sides irradiated). The conductivity levels off after ~ 20 minutes; further irradiation produces no additional change in conductivity. To confirm that this plateau corresponds to complete reaction throughout the

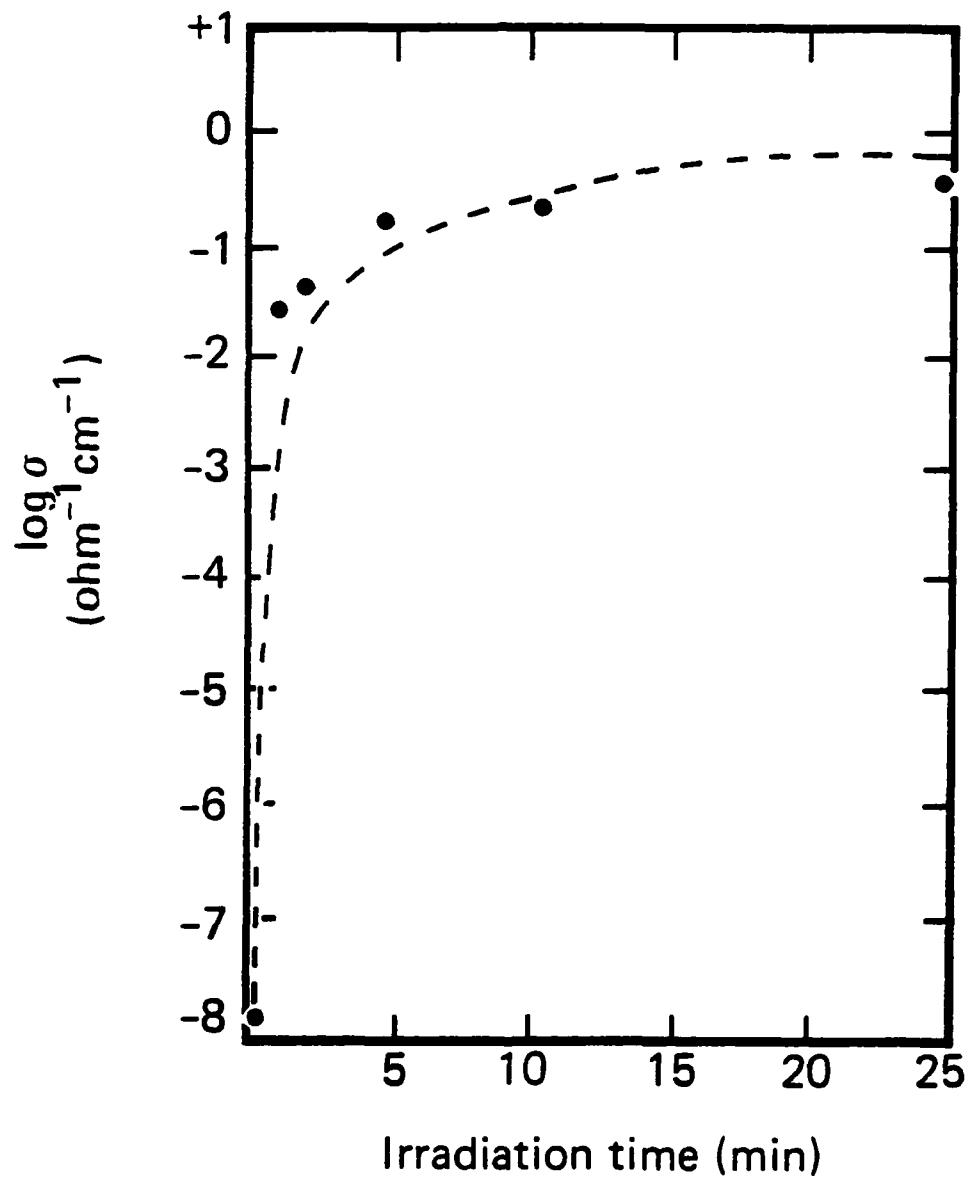
bulk of the film, a different sample was covered on one side and irradiated from the other. Four point probe measurements at successive time intervals showed that, as expected, the apparent conductivity on the covered side was considerably lower than that of the exposed side in the early stages of irradiation, but that after ~ 40 minutes both sides showed essentially equal conductivities. As hoped, masking given areas of the film from the incident radiation leads to doping only in the exposed areas. Unreacted salt in the undoped areas can be subsequently removed with a methylene chloride wash.

Perhaps the most valuable aspect of this technique is the control which it affords over the final doping level, particularly in the low doping regime where reproducible results are rather difficult to obtain with the conventional gas phase dopants. Figure 2 shows the results obtained by simply dipping the $(CH)_x$ films into methylene chloride solutions containing varying concentrations of triphenylsulfonium hexafluoroarsenate, drying, and then irradiating to completion. As expected, the final conductivity scales quite reproducibly with the initial solution concentration. We are continuing our investigation of this useful technique.

We thank the Office of Naval Research for partial support of this work.

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Conductivity as a function of irradiation time for $(\text{CH})_x$ film treated with 1 molar solution of triphenylsulfonium hexafluoroarsenate in methylene chloride.

Figure 1.

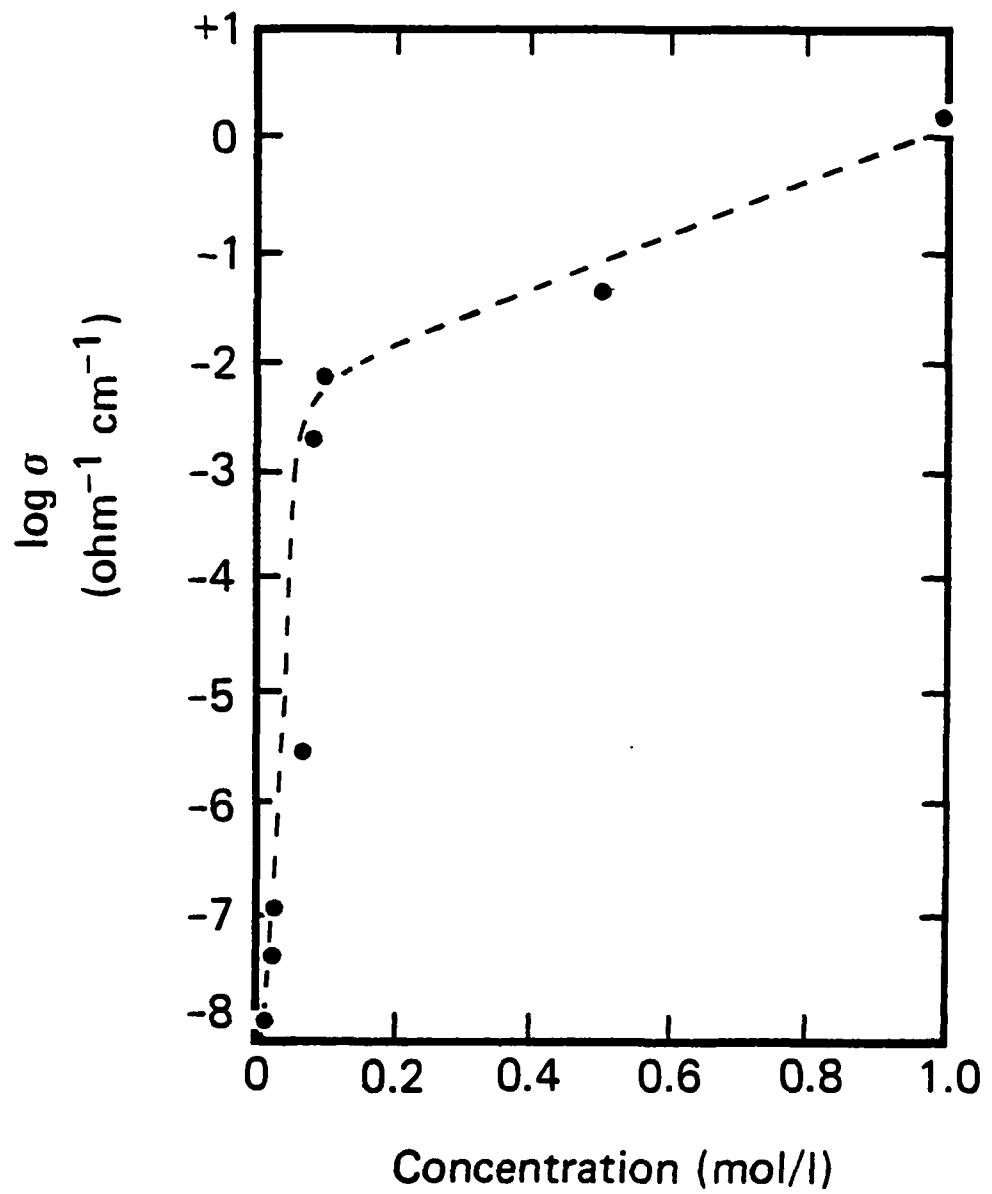


Figure 2. Conductivity after 20 min. irradiation for $(CH)_x$ films treated with varying concentrations of triphenylsulfonium hexafluoroarsenate in methylene chloride.